PHOTOREACTIVE TITANATE NANOMATERIALS FOR WATER PURIFICATION SYSTEMS

By

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CERTIFICATE OF AUTHORSHIP

I certify that the work in this thesis has not previously been submitted for a degree, nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that this thesis has been written by me. Any help that I have received in my research work on the preparation of the thesis itself has been acknowledged. In addition, I certify that all the information sources and literature used as indicated in the thesis.

Signature of Candidate

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I dedicate this work to my parents in Lebanon

Jihad & Jamilee El Saliby

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ABSTRACT

Increasing water scarcity and environmental considerations are calling for more effective means to purify industrial and urban wastewaters. Advanced oxidation processes are able to effectively remove many persistent and toxic pollutants from water to enable the use and reuse of impaired quality raw water sources. Among these processes, heterogeneous photocatalysis has some notable inherent advantages, such as relative process simplicity, and the minimal generation of waste streams. Unfortunately, the commercially available photocatalysts show poor efficiency in the utilisation of natural solar radiation and are difficult to separate and recover from treated water, which results in high operational costs. In order to alleviate these recognised problems, this thesis explored an improved method of material synthesis to produce nanomaterials with desirable properties.

The investigation of peroxide method at high pH values showed that this facile approach offers great potential for the fabrication of various nanoparticles, nanostructures, and thin films deposits. The shape, size, structure and surface properties of the resulting photocatalysts were simply controlled through the process pH, the time of reaction, and the chemical composition of the solvent base. Both partial and complete dissolution of the precursors was accomplished to fabricate various, crystalline and amorphous anatase and alkali titanate end products. The use of ammonium hydroxide base was more advantageous, since it provided a very simple means to achieve simultaneous N doping.

Effective N-doping of Degussa P25 commercial photocatalyst was simply achieved using highly concentrated (25%) ammonium hydroxide base in 24 h time at room temperature in an open reactor. The raw product slurries were neutralised with acid, washed with water, and aged until dry at 75 °C. Additional doping (co-doping) with Ag was achieved by adding $AgNO_3$ to the raw slurries. The resulting nanoparticles had elongated rod and needle-like shapes, 2-3 times larger specific surface area (92.9-144.6 m^2g^{-1}) than the precursor P25, and 5.4-6.5 nm mesopore sizes. These photocatalysts were remarkably effective in the photobleaching of Methylene Blue

under visible light, and simulated solar light illuminations. Therefore, this method is suitable to improve the performance of currently available commercial photocatalysts.

Na-titanate microspheres with 700-800 nm diameter were produced at low (25-80 $^{\circ}$C) temperatures using NaOH for base, and P25 precursor in the peroxide method. Both the raw and calcined products showed very high adsorption affinity towards Methylene Blue dye, and were also capable of its degradation under UV light without minimal loss of performance after five complete treatment cycles. The calcined product showed higher catalytic activity, and could be fully recovered from the spent slurry by gravity settling.

Exchanging Na with H in titanates microspheres in HCl solution resulted in the formation of hydrogen-titanate nanofibres, which were transformed into anatase nanofibres after annealing at 550 °C for 6 h. The nanofibres had average specific surface area of 31.5 m^2/g, average pore volume of 0.10 cm^3/g and average pore size of 50 Å. These products also were effective adsorbent of the model pollutant and adsorbents and good photocatalyst under simulated solar light illumination. No reduction in photocatalytic activity was observed over three complete treatment cycles, and the effective separation of nanofibres was achieved by gravity settling resulting in low residual solution turbidity. Such nanofibres may also be used to produce paper-like photoreactive filter materials.

An easily separable fibrous photocatalyst was produced by depositing H-titanate nanofibres on wool fibres serving as bio-template. The calcined end-product showed anatase crystal phase and nanofibrous morphology (about 50 µm length and 9.5 µm diameter), having about 24 m^2/g specific surface area with mesoporous characteristics. These nanofibres were effective in the photocatalytic degradation of humic acid model pollutant solution under UV light irradiation. The performance of this photocatalyst showed only a small decrease after three complete treatment cycles, and the microfibres were easily separated from the treated solution by sedimentation with very low supernatant turbidity.